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Crystal structures of $Ph_2PbCl_2(imidazole)_2$ isomers with *trans*- and *cis*-arrangements of the phenyl groups

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Abstract

The isomers of the $Ph_2PbCl_2(imidazole)_2$ complex having *trans*- and *cis*-arrangements, respectively, of the phenyl groups have been prepared and subjected to X-ray diffraction studies. The *trans*-complex has an almost regular octahedral environment for its lead atom. In the *cis*-complex the coordination octahedron is strongly distorted, with the C–Pb–C and N–Pb–N angles of 129° and 59°, respectively. The molecules are associated through hydrogen bonds N–H···Cl into layers (*trans*-complex) or chains (*cis*-complex).

Key words: Lead; Hydrogen bonding; Imidazole; X-ray diffraction

1. Introduction

In 1987 it was shown that, depending on the nature of the solvent, the complex of the composition $(p\text{-}ClPh)_2SnCl_2(4,4'\text{-}Me_2dipy)$ could be obtained in either of two isomeric forms with *cis*- and *trans*-arrangements respectively of phenyl groups [1]. At about the same time some of us carried out an X-ray structural study on several organolead compounds, and in particular on Ph_2PbCl_2dipy [2]. In continuation of this work we have studied complexes of Ph_2PbCl_2 with imidazole and have found that *cis-trans* isomers can be isolated in this case also.

2. Experimental details

2.1. Synthesis and crystal preparation

Ph_2PbCl_2 (0.5 g) was treated with a two-fold excess of imidazole in 40 ml of the boiling solvent. In the case of the *cis*-complex the solvent was 1,2-dichloroethane and the crystals were grown by slow cooling. The *trans*-complex was made in acetone solution and the crystals obtained by evaporation at 20°C.

2.2. Crystal data

trans-$C_{18}H_{18}N_4Cl_2Pb$: M = 568.5, monoclinic, space group $P2_1/n$, $a = 9.285(2)$, $b = 13.355(3)$, $c = 16.916(4)$ Å, $\beta = 106.30(2)°$, $v = 2013$ Å^3, $Z = 4$, $D_c = 1.875$ g/cm^3, $\mu = 87.2$ cm^{-1} (Mo Kα radiation).

cis-$C_{18}H_{18}N_4Cl_2Pb$: M = 568.5, triclinic, space group $P\bar{1}$, $a = 9.268(2)$, $b = 9.276(2)$, $c = 13.004(3)$ Å, $\alpha = 108.77(2)°$, $\beta = 102.19(2)°$, $\gamma = 73.27(2)°$, $v = 1005$ Å^3, $Z = 2$, $D_c = 1.878$ g/cm^3, $\mu = 87.3$ cm^{-1} (Mo Kα radiation).

2.3. Data collection and structure determination

Colourless single crystals of approximate dimensions 0.2 × 0.2 × 0.35 mm (*trans*) and 0.25 × 0.25 × 0.25 mm (*cis*) mounted on glass fibres were used with an Enraf-Nonius CAD-4 diffractometer (graphite monochromator, ω-scanning). For structure determinations and refinement 3233 (*trans*) and 2031 (*cis*) reflections with $\theta_{max} = 30°$ and 25° and with $I > 3\sigma(I)$ were used. Absorption corrections using ψ-scanning curves of 10 reflections were applied. The positions of the lead atoms were determined by the Patterson method, and the other atoms were found from Fourier and difference Fourier syntheses. The hydrogen atoms were placed in calculated positions and included in the structure factor calculations but not refined. All non-hydrogen

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TABLE 1. Fractional atomic coordinates for *trans*- and *cis*-$Ph_2PbCl_2(imidazole)_2$ ($\times 10^5$ for Pb in *trans*; $\times 10^4$ for Cl, N, C in *trans* and for Pb and Cl in *cis*, $\times 10^3$ for N and C in *cis*)

Atom	*trans*			*cis*		
	x	*y*	*z*	*x*	*y*	*z*
Pb	6(3)	12939(2)	25473(1)	2499(2)	2500(2)	2467(1)
C1(1)	−2630(2)	980(1)	1389(1)	−201(7)	4530(7)	2222(6)
C1(2)	2590(2)	1592(2)	3727(1)	5174(7)	1047(9)	3411(5)
N(1)	237(7)	2924(4)	1870(4)	268(2)	186(3)	53(2)
C(1)	1151(9)	3691(6)	2125(5)	359(3)	70(4)	−12(2)
N(2)	944(9)	4382(6)	1518(5)	334(4)	85(4)	−113(2)
C(2)	−141(8)	4020(8)	844(6)	192(4)	284(3)	−8(2)
C(3)	−559(9)	3113(7)	1058(5)	228(4)	226(5)	−112(2)
N(3)	−245(7)	−326(4)	3191(4)	230(3)	−9(3)	124(2)
C(4)	−1052(8)	−1125(7)	2883(5)	150(3)	−47(3)	25(2)
N(4)	−964(8)	−1811(5)	3484(5)	160(3)	−205(3)	−9(2)
C(5)	−120(9)	−1425(8)	4197(6)	290(5)	−143(3)	155(3)
C(6)	379(9)	−493(8)	4019(6)	243(5)	−266(4)	76(3)
C(11)	1228(7)	626(5)	1758(4)	132(3)	202(3)	358(2)
C(12)	2608(8)	1030(6)	1764(5)	194(3)	221(3)	466(2)
C(13)	3375(9)	590(8)	1231(5)	118(3)	191(3)	537(2)
C(14)	2761(9)	−212(7)	740(5)	−16(4)	141(3)	496(2)
C(15)	1381(9)	−614(7)	754(5)	−76(4)	124(4)	387(3)
C(16)	609(8)	−188(6)	1274(5)	−2(2)	153(3)	315(2)
C(21)	−1228(7)	1984(5)	3325(4)	368(2)	433(3)	278(2)
C(22)	−2534(8)	1544(7)	3389(5)	308(4)	581(3)	339(2)
C(23)	−3285(9)	1984(8)	3932(5)	382(4)	702(4)	355(3)
C(24)	−2739(9)	2861(7)	4348(5)	512(3)	668(3)	309(3)
C(25)	−1435(9)	3305(6)	4255(5)	574(3)	517(3)	251(2)
C(26)	−673(8)	2861(5)	3734(4)	504(3)	397(3)	239(3)

TABLE 2. Selected bond lengths (Å) and angles (°) in *trans*- and *cis*-$Ph_2PbCl_2(imidazole)_2$

	trans	*cis*		*trans*	*cis*
Pb–Cl(1)	2.701(2)	2.692(6)	C(1)–N(2)	1.35(1)	1.34(4)
Pb–Cl(2)	2.689(2)	2.707(6)	N(2)–C(2)	1.38(1)	1.39(5)
Pb–N(1)	2.498(7)	2.43(2)	C(2)–C(3)	1.35(1)	1.36(4)
Pb–N(3)	2.461(7)	2.46(2)	N(3)–C(4)	1.32(2)	1.34(3)
Pb–C(11)	2.175(8)	2.20(3)	N(3)–C(6)	1.37(2)	1.35(4)
Pb–C(21)	2.173(7)	2.16(3)	C(4)–N(4)	1.35(1)	1.37(3)
N(1)–C(1)	1.33(2)	1.33(3)	N(4)–C(5)	1.34(1)	1.38(5)
N(1)–C(3)	1.39(1)	1.35(4)	C(5)–C(6)	1.39(2)	1.37(5)
Cl(1)PbCl(2)	178.66(7)	160.9(2)	PbN(1)C(1)	131.0(5)	132(2)
Cl(1)PbN(1)	88.9(1)	90.7(5)	PbN(1)C(3)	121.4(5)	122(2)
Cl(1)PbN(3)	90.4(1)	108.2(5)	C(1)N(1)C(3)	107.3(7)	105(3)
Cl(1)PbC(11)	90.8(2)	80.9(6)	C(1)N(2)C(2)	107.6(8)	107(3)
Cl(1)PbC(21)	89.0(2)	90.8(6)	PbN(3)C(4)	130.3(5)	129(2)
Cl(2)PbN(1)	92.1(1)	107.2(5)	PbN(3)C(6)	121.9(5)	123(2)
Cl(2)PbN(3)	88.6(1)	87.2(5)	C(4)N(3)C(6)	107.5(8)	107(2)
Cl(2)PbC(11)	90.2(2)	89.0(6)	C(4)N(4)C(5)	108.1(8)	107(2)
Cl(2)PbC(21)	90.0(2)	82.9(6)	N(1)C(1)N(2)	109.9(6)	111(3)
N(1)PbN(3)	179.0(2)	59.4(9)	N(2)C(2)C(3)	106.9(8)	105(3)
N(1)PbC(11)	87.0(2)	140.5(8)	N(1)C(3)C(2)	108.3(7)	111(3)
N(1)PbC(21)	92.2(2)	89.3(9)	N(3)C(4)N(4)	110.0(7)	109(2)
N(3)PbC(11)	92.3(2)	86.6(9)	N(4)C(5)C(6)	107.2(8)	106(3)
N(3)PbC(21)	88.7(2)	142.5(9)	N(3)C(6)C(5)	107.2(8)	110(3)
C(11)PbC(21)	179.0(2)	129.1(8)			

atoms were refined anisotropically. Refinement led to the final residuals $R = 0.029$ (*trans*) and 0.051 (*cis*). Structure determinations were carried out with the SDP package [3], and geometrical calculations were performed by use of the PARST program [4]. For the *trans*-complex ordinary full-matrix refinement led to a model with markedly different lengths for chemically equivalent bonds; thus in one of the phenyl rings $d(C\text{–}C)_{av}$ was 1.30 Å and in the other it was 1.50 Å [5]. We judged that this approach was unsuccessful by virtue of the particular position of the lead atom: its coordinates were very close to 0, 1/8, 1/4 and hence the contribution of this atom to reflections with odd h + k was small. In the initial stages of the structure determination the inaccuracies in the lead atom coordinates led to significant errors in calculated structure factors and to distortions of the Fourier map. In view of this we placed constraints on the Pb–Cl, Pb–N and Pb–C distances and used fixed geometries for the phenyl and imidazole rings in the initial stages, and the

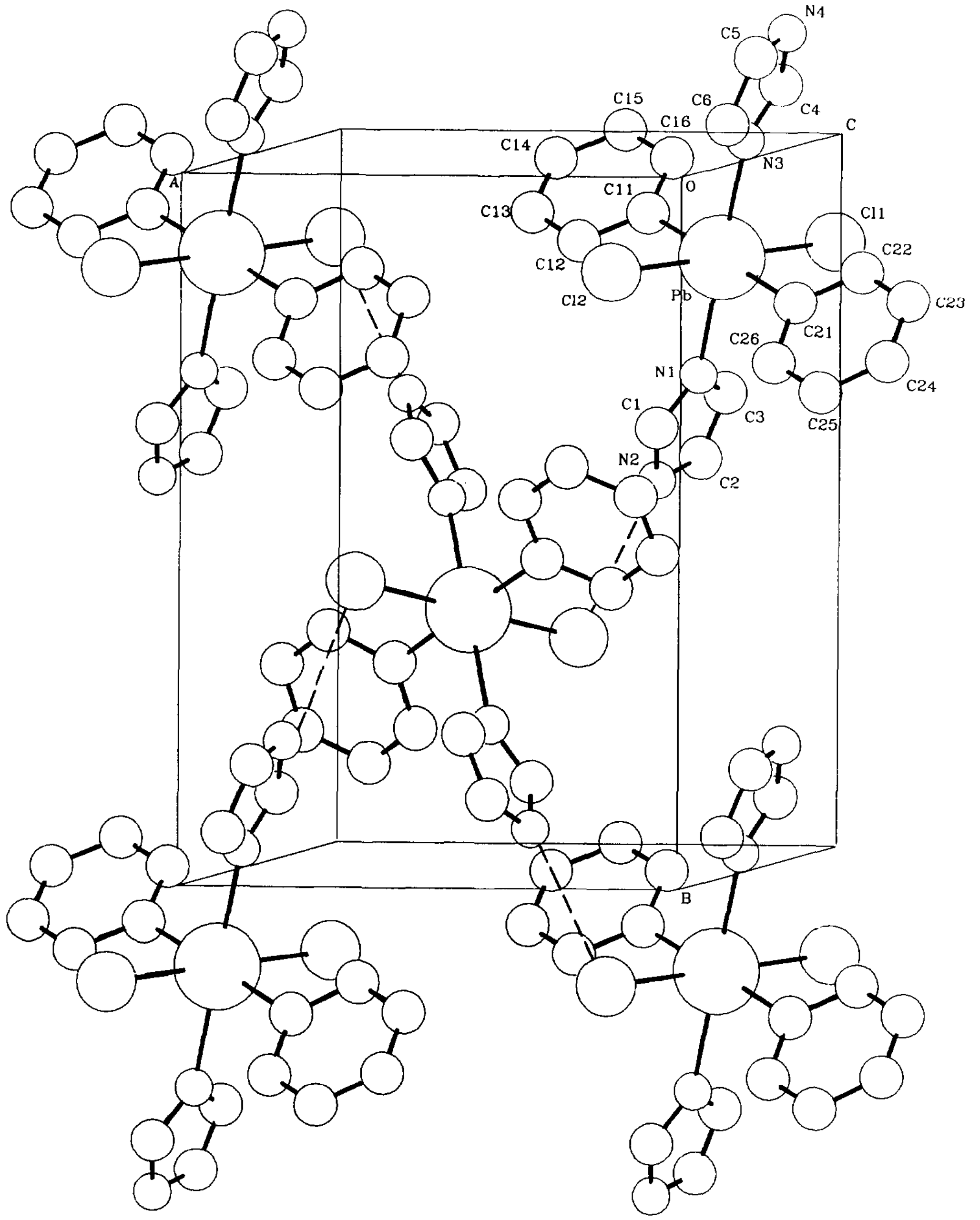

Fig. 1. Packing diagram for *trans*-$Ph_2PbCl_2(imidazole)_2$.

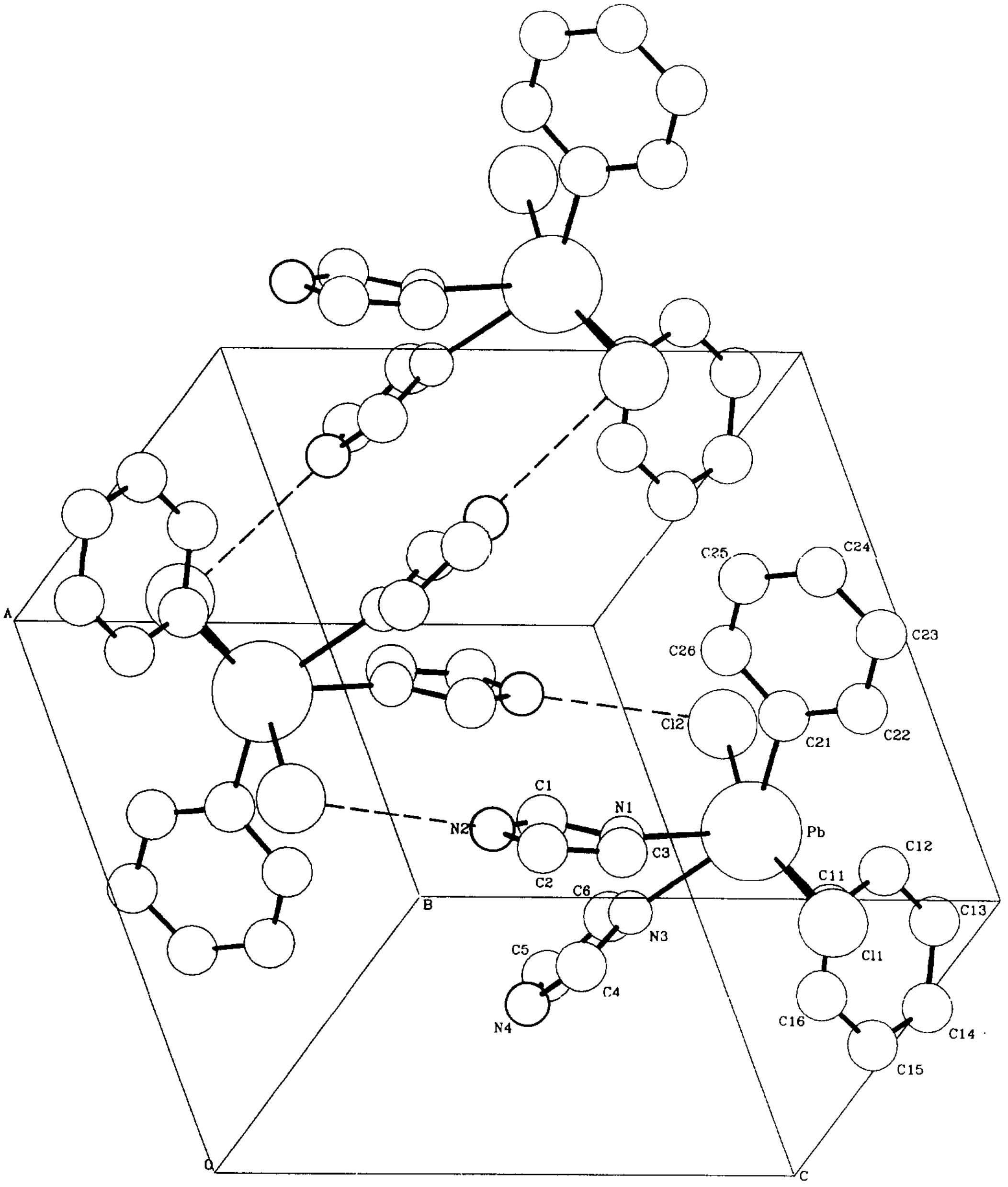

Fig. 2. Packing diagram for *cis*-$Ph_2PbCl_2(imidazole)_2$.

ordinary full-matrix procedure without any constraints at the stage of anisotropic refinement. Final fractional atomic coordinates are given in Table 1, bond distances and angles in Table 2. A complete list of bond lengths and angles and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

In the *trans*-complex the lead atoms have an almost regular octahedral environment. The coordination octahedron of the *cis*-complex is distorted more strongly than in the corresponding *cis*-$(p\text{-}ClPh)_2SnCl_2(4,4'\text{-}Me_2dipy)$: the angle C–Pb–C is 13° larger and the angle N–Pb–N 10° smaller than the corresponding C–Sn–C and N–Sn–N angles. The rigidity of the dipy ligand probably prevents further distortions of angles in the tin complex. Another distinct feature of the *cis*-complex is the bending of the Pb–Cl bonds towards the phenyl groups, the Sn–Cl bonds in the corresponding tin complex being bent away from the phenyl groups. This may be due to steric strain in the PbN_2C_2

TABLE 3. Details of NH ··· Cl hydrogen bonds in the structures of *trans*- and *cis*-$Ph_2PbCl_2(imidazole)_2$ (H atoms were placed in calculated positions, d(N–H) = 1.04 Å)

Atoms	N ··· Cl	H ··· Cl	N–H ··· Cl	Pb–Cl ··· H
trans-complex				
N(2)–H(2) ··· Cl(2) ^{1}	3.325	2.31	165	91
N(4)–H(4) ··· Cl(1) ^{2}	3.257	2.24	165	93
cis-complex				
N(2)–H(2) ··· Cl(2) ^{3}	3.28	2.27	164	93
N(4)–H(4) ··· Cl(1) ^{4}	3.27	2.26	163	92

Atomic coordinates are produced by the following symmetry operations: ^{1} $1/2-x, 1/2+y, 1/2-z$; ^{2} $-1/2-x, -1/2+y, 1/2-z$; ^{3} $1-x, 1-y, 1-z$; ^{4} $-x, 1-y, 1-z$.

plane (which is slightly puckered) and to the presence of hydrogen bonds, as discussed below. The bond lengths in the coordination sphere of the lead atom are practically equal for the *trans*- and *cis*-complexes; the Pb–N distances may be slightly shorter in the *cis*-complex, but the difference is at the level of the esd. In the Ph_2PbCl_2dipy complex, which is very similar to its tin analogue [6], the Pb–Cl distances are 0.06 Å shorter, and the Pb–N distances 0.04–0.07 Å longer than those in the structures investigated here. The Pb–C bonds in the *trans*- and *cis*-complexes and in Ph_2PbCl_2dipy (2.16–2.18 Å) are significantly shorter than those in four-coordinated organolead compounds such as $PbPh_4$ [2] or Pb_2Ph_6 [7] (2.21–2.22 Å). Molecules of the complexes are associated in the crystals through NH ··· Cl hydrogen bonds, the parameters for which are listed in Table 3. The *cis*-molecules are associated into zigzag chains directed along the *a* axis, and the *trans*-molecules form layers perpendicular to the *c* axis, as can be seen from Figs. 1 and 2. It is known that the H atom on the amino-nitrogen atom of imidazole has a relatively high acidity due to charge delocalization from the amino to the imino N atom. Complex formation involving ligation through the latter atom stabilizes the resonance form with the excess of charge on this atom and at the same time removal or bonding of a proton from the amino group increases the electron-donating ability of the imino nitrogen, and so formation of hydrogen bonds is usual for the range of imidazole complexes. In our case the H ··· Cl interactions lead also to the weakening of Pb–Cl bonds. Complex formation causes the angles at the imino and amino nitrogens to become equal; in the more accurately determined structure for the *trans*-complex they are 107.4 and 107.8°, compared with values of 105.1 and 107.1° in pure imidazole [8] and 109.1° in the imidazolium cation [9].

Despite the fact that the shapes of *cis*- and *trans*-complex molecules are very different, the densities and volumes per molecule are practically the same for the two isomers. The hydrogen bonding parameters are also very similar. Thus the predominance of one or the other isomer can be due only to the difference in the stabilities of the individual molecules. From consideration of the structure and shape of the *trans*- and *cis*-molecules it seems likely that *trans*-molecules can be solvated effectively in polar solvents. In contrast the *cis*-molecules involve steric strain, but they can form dimers and higher aggregates through hydrogen bonding in non-polar solvents. The limiting case of such association is the formation of the chains in the crystal structure of the *cis*-complex (see Fig. 2).

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